TITLE OF THE INVENTION

Superconducting Ceramics

BACKGROUND OF THE INVENTION

This invention relates to superconducting ceramics having a high critical temperature.

The prior art has proposed the use of metals such as mercury and lead, intermetallics such as NbNd, Nb_3Ge and Nb_3Ga and ternary materials such as $Nb_3(Al_{0.8}Ge_{0.2})$ as superconductors. Another type of superconducting material, superconductive barium-lead-bismuth oxides, is described in US Patent 3,932,315. However, only three-dimensional electron conduction takes place in such conventional superconducting materials, and the critical transition temperature (Tc) of such conventional superconducting materials cannot therefore exceed $25^{o}K$.

In recent years, superconducting ceramics have attracted widespread interest. A new material was first reported by researchers at the Zurich laboratory of IBM Corp. as Ba-La-Cu-O-type high temperature superconducting oxides. Also, La-Sr-Cu(II)-O-type superconducting oxides have been proposed. This type of superconducting material appears to form a quasi-molecular crystalline structure whose unit cell is constructed with one layer in which electrons have

essentially one-dimensional motion. Such a superconducting material, however, has Tc lower than $30^{o}K$.

OBJECTS AND SUMMARY OF THE INVENTION

The present invention seeks to provide superconducting ceramics having a higher Tc than hitherto, and having few defects and a smaller interfacial area in its polycrystalline structure.

In accordance with the invention, there is provided a superconducting ceramic material which, in its broadest aspect, can be represented by the general formula

$$(A_{1-x}B_x)_y\ Cu_z\ O_w \qquad (i)$$

in which $0.1 \leqslant \underline{x} < 1$

$\underline{y} = 2.0-4.0$

$\underline{z} = 1.0-4.0$

$\underline{w} = 4.0-10.0$

A is one or more rare earth elements and

B is more than one alkaline earth element when A is one rare earth element, and is one or more alkaline earth elements when A is more than one rare earth element.

In general formula (i), preferably

$\underline{y} = 2.5-3.5$

$\underline{z} = 1.5-3.5$ and

$\underline{w} = 6.0-8.0$.

The general formula (i) above embraces several sub-species of superconducting ceramic materials. One of these can be represented by the general formula

$$(A_{1-x}B_x)_yCu_zO_w.(A_{1-x'}B'_{x'})_{y'}Cu_{z'}O_{w'} \qquad (ii)$$

in which $0.1 \leq \underline{x} < 1$

$0.1 \leq \underline{x}' < 1$

$\underline{y}$ = 2.0-4.0, preferably 2.5-3.5

$\underline{y}'$ = 2.0-4.0, preferably 2.5-3.5

$\underline{z}$ = 1.0-4.0, preferably 1.5-3.5

$\underline{z}'$ = 1.0-4.0, preferably 1.5-3.5

$\underline{w}$ = 4.0-10.0, preferably 6.0-10.0

$\underline{w}'$ = 4.0-10.0, preferably 6.0-8.0

A is one or more rare earth elements and

B and B' are two or more alkaline earth elements.

Within the materials of general formula (ii), there are those in which A is one rare earth element exemplified by $YbBaSrCu_3O_{6-8}$, $YBaCaCu_3O_{6-8}$ and $YbBa_{0.7}Sr_{0.7}Ca_{0.6}Cu_3O_{6-8}$; and those in which A is more than one rare earth element exemplified by $Y_{0.5}Yb_{0.5}BaSrCu_3O_{6-8}$ and $Y_{0.5}Yb_{0.5}BaCaCu_3O_{6-8}$.

Another sub-species of superconducting ceramic materials of the general formula (i) can be represented by the general formula

$$[\, A_{1-x}(B_{1-q}B'_{q})_{x} \,]_{y}Cu_{z}O_{w} \qquad \text{(iii)}$$

in which $0.1 \leq \underline{x} < 1$

$0 < \underline{q} < 1$

$\underline{y} = 2.0\text{-}4.0$, preferably 2.5-3.5

$\underline{z} = 1.0\text{-}4.0$, preferably 1.5-3.5

$\underline{w} = 4.0\text{-}10.0$, preferably 6.0-8.0

A is a rare earth element and

B and B' are different alkaline earth elements.

A further sub-species can be represented by the general formula

$$[\, (A_{1-p}A'_{p})_{1-x}(B_{1-q}B'_{q})_{x} \,]_{y}Cu_{z}O_{w} \qquad \text{(iv)}$$

in which $0.1 \leq \underline{x} < 1$

$0 < \underline{p} < 1$

$0 < \underline{q} < 1$

$\underline{y} = 2.0\text{-}4.0$, preferably 2.5-3.5

$\underline{z} = 1.0\text{-}4.0$, preferably 1.5-3.5

$\underline{w} = 4.0\text{-}10.0$, preferably 6.0-8.0

A and A' are different rare earth elements and

B and B' are different alkaline earth elements.

Yet another sub-species can be represented by the general formula

$$[(A_{1-p}A'_{p})_{1-x}B_{x}]_{y}Cu_{z}O_{w} \qquad (v)$$

in which

$0.1 \leq \underline{x} < 1$

$0 < \underline{p} < 1$

$\underline{y}$ = 2.0-4.0, preferably 2.5-3.5

$\underline{z}$ = 1.0-4.0, preferably 1.5-3.5

$\underline{w}$ = 4.0-10.0, preferably 6.0-8.0

A and A' are different rare earth elements

and

B is an alkaline earth element.

Examples of materials of the general formula (v) are $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6-8}$ and $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{6-8}$.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a perspective view showing a perovskite-like structure superconducting ceramic.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the above general formulae except where otherwise specified or where the context does not permit each of A, A', B and B' is used collectively, that is to say A may represent any number of rare earth elements A_1, A_2, A_3......A_n, and so on.

The term "rare earth elements" used herein should be given the same meaning as that in "Chambers Dictionary of Science and Technology", that is, the lanthanide elements of atomic numbers 57 to 71, together with scandium (atomic no.21) and yttrium (atomic

no.39), namely, La, Ce, Pr, Nb, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y. The alkaline earth metals are those belonging to Group 2A of the Periodic Table, namely, Be, Mg, Ca, Sr, Ba, and Ra.

Superconducting materials have a perovskite-like structure a unit cell of which is illustrated schematically in Fig.1 of the accompanying drawings. In the figure, copper atoms 2 and 8 are each surrounded by five oxygen atoms 5 in a pyramidal arrangement; between the two pyramids, a central copper atom 3 is surrounded by four oxygen atoms (two of which form the apices of the oxygen pyramids around the copper atoms 2 and 8) and two vacant positions 7. The atoms of rare earth elements 1 are situated at the corners of the unit cell and the atoms of alkaline earth metals 4 are situated along the edges of the unit cell. The structure shown in the figure may be considered to represent $(YBa_2)Cu_3O_{7-x}$. In this structure, superconductivity results from the electrons in the layer-like structure which is formed by the four oxygen atoms surrounding each central copper atom 3.

The superconducting ceramics in accordance with the invention, in common with prior art superconducting ceramics, have such a perovskite-like structure. However, two or more rare earth elements and/or two or

more alkaline earth elements are used, so that poly-crystalline structures are formed together forming a number of large crystalline particles. In this manner, Tc is elevated because of the reduced area of the interfaces between crystalline particles. Of course, the ideal structure is a single-crystal.

Superconducting ceramics can be very easily produced. For example, firstly, in accordance with the prescribed stoichiometry oxides, and carbides if necessary, whose purity is 99.9% or 99.99%, are ground in a ball mill to a powder and mixed together. Next, the powder is pressed to a tablet and then finely ground and pressed to a tablet again. Finally, the tablet is sintered at an elevated temperature.

The following Examples illustrate the invention. Although the Examples do not include all the combinations of elements which may be used to produce the materials of the invention, other combinations are also effective to constitute improved superconducting materials.

EXAMPLE 1

Y_2O_3, $BaCO_3$, $CaCO_3$ and CuO all in the form of fine powders having a purity of 99.95% or higher were mixed in the proportions required by formula (ii) with $\underline{x}$ = 0.67 (A:B=1:2); $\underline{x}'$ = 0.33 (A:B'=2:1); $\underline{y}$ = 1.0; $\underline{y}'$ =

1.0; $\underline{z}$ = 3.0; $\underline{z}'$ = 3.0; $\underline{w}$ = 6 to 8; and $\underline{w}'$ = 6 to 8 with A being yttrium, B being barium and B' being calcium (B:B'=1:1). These materials were thoroughly mixed in a mortar, packed into capsules and pressed in the form of tablets of 10 mm diameter and 3 mm thickness. Then, the tablets were baked for 8 hours at 500-900°C, for example 700°C, in oxidizing surroundings, for example ambient air.

The tablets were then ground in a mortar to a powder with an average particle radius of less than 10 µm. The powder was pressed again in capsules under a pressure of 50kg/cm^2 at an elevated temperature to form tablets. The tablets were baked for 10-50 hours, for example 15 hours, at 500-900°C, for example 900°C in oxidizing surroundings, for example ambient air. Finally, the tablets were reduced by heating for 3-30 hours, for example 20 hours at 600-1100°C, for example 800°C in an oxygen/argon mixture containing a minor proportion of oxygen. Eventually, a new structure was observed. This material can be represented by the stoichiometric formula $YBaCaCu_3O_{6-8}$.

The relationship between the temperature and the resistivity of this material in tablet form was investigated. It was observed that the phase transition to the superconducting state began as the

temperature descended below $104^{o}K$(Tc onset temperature) and the disappearance of resistance was observed at $93^{o}K$(Tco).

EXAMPLE 2

Yb_2O_3, $BaCO_3$, Sr_2O_3 and CuO all in the form of fine powders having a purity of 99.95% or higher were mixed in the proportions required by formula (ii) with $\underline{x}$ = 0.67 (A:B=1:2); $\underline{x}'$ = 0.33 (A:B=2:1); $\underline{y}$ = 1.0; $\underline{y}'$ = 1.0; $\underline{z}$ = 3.0; $\underline{z}'$ = 3.0; $\underline{w}$ = 6 to 8; and $\underline{w}'$ = 6 to 8 and with A being ytterbium, B being barium and B' being strontium (B:B'=1:1). The procedure described in example 1 was followed and the resulting material can be represented by the stoichiometric formula $YbBaSrCu_3O_{6-8}$.

The relationship between the temperature and the resistivity of this material in tablet form was investigated. The phase transition to superconductivity was observed when the temperature descended below $109^{o}K$(Tc onset temperature) and the disappearance of resistance was observed at $37^{o}K$(Tco).

EXAMPLE 3

The procedure of Example 2 was repeated but with 30% of Ba and Sr substituted by Ca (introduced as $CaCO_3$). As a result, Tc onset was elevated further by $3\text{-}5^{o}K$. The material obtained can be represented by the stoichiometric formula $YbBa_{0.7}Sr_{0.7}Ca_{0.6}Cu_3O_{6-8}$.

EXAMPLE 4

Y_2O_3, Yb_2O_3, $BaCO_3$, $CaCO_3$ and CuO all in the form of fine powders having a purity of 99.95% or higher were mixed in the proportions required by formula (ii) with x = 0.33 (A:B=2:1); x' = 0.66 (A:B=1:2); y = 1.0; y' = 1.0; z = 3.0; z' = 3.0; w = 6 to 8; and w' = 6 to 8 with A being yttrium, A' being ytterbium, B being barium and B' being calcium (B:B'=1:1; A:A' = 1:1, 1:2, or 1:5). These materials were thoroughly mixed in a mortar, packed into capsules and pressed ($3kg/cm^2$) in the form of tablets of 10 mm diameter and 5 mm thickness. Then, the tablets were baked for 8 hours at 500-1000°C, for example 700°C in oxidizing surroundings, for example ambient air.

The tablets were then ground in a mortar to a powder with an average particle radius of less than 10 µm. The powder was pressed again in capsules under a pressure of $50kg/cm^2$ at 300-800°C to form tablets. The tablets were baked for 10-50 hours, for example 15 hours at 500-900°C, for example 900°C in oxidizing surroundings, for example in ambient air. In addition to the conventional perovskite-like structure, a different structure was also observed in this tablet. Finally, the tablets were reduced by heating for 3-30 hours, for example 20 hours at 600-1100°C, for example 800°C in an oxygen/argon mixture containing a minor

proportion of oxygen. Eventually, a new structure was clearly observed. This material can be represented by the stoichiometric formula $Y_{0.5}Yb_{0.5}BaCaCu_3O_{6-8}$.

The relationship between the temperature and the resistivity of this material in tablet form was investigated. Phase transition to superconductivity was observed when the temperature descended below 107°K and the disappearance of resistance was observed at 101°K(Tco).

EXAMPLE 5

The procedure of Example 4 was repeated but using in place of ytterbium and barium, gadolinium (as Gd_2O_3) and strontium and $\underline{x}:\underline{x}'=1:1$ and $\underline{y}:\underline{y}'=1:1$. Tc onset and Tco were observed at 104°K and at 84°K, respectively. This material can be represented by the stoichiometric formula $Y_{0.5}Yb_{0.5}BaSrCu_3O_{6-8}$.

EXAMPLE 6

The procedure of Example 4 was repeated but with 30% of Y and Yb substituted by Nb(introduced as Nb_2O_3). Tc onset was elevated further by 3-5°K.

EXAMPLE 7

Yb_2O_3, Y_2O_3, $BaCO_3$, Sr_2O_3 and CuO all in the form of fine powders having a purity of 99.95% or higher were mixed in the proportions required by formula (i) with $\underline{x}$ = 0.67 (A:B=1:2); $\underline{y}$ = 1.0; $\underline{z}$ = 3.0; and $\underline{w}$ = 6 to

8 with A being yttrium and ytterbium, and B being barium (Y:Yb being 1:1, 1:2 or 1:5). These materials were thoroughly mixed in a mortar, packed into capsules and pressed ($3kg/cm^2$) in the form of tablets of 10 mm diameter and 3 mm thickness. Then, the tablets were baked for 8 hours at 500-1000°C, for example 700°C in oxidizing surroundings, for example ambient air.

The tablets were then ground in a mortar to a powder with an average particle radius of less than 10 µm. The powder was pressed again in capsules under a pressure of $50kg/cm^2$ at 300-500°C, for example 400°C to form tablets. The elevation of temperature is advantageous in reducing defects in the tablets. Then, the tablets were baked and oxidized for 10-50 hours, for example 15 hours at 500-1000°C, for example 900°C in oxidizing surroundings, for example ambient air. Finally, the tablets were reduced by heating for 3-30 hours, for example 20 hours at 600-1100°C, for example 800°C in an oxygen/argon mixture containing a minor proportion of oxygen. Eventually, a new structure was observed clearly. This material can be represented by the stoichiometric formula $Y_{0.5}Yb_{0.5}Ba_2Cu_3O_{6-8}$.

The relationship between the temperature and the resistivity of this material in tablet form was investigated. Phase transition to superconductivity

was observed when the temperature descended below 105^{o}K(Tc onset temperature) and the disappearance of resistance was observed at 89^{o}K(Tco).

EXAMPLE 8

The procedure of Example 7 was repeated but using in place of ytterbium, gadolinium (as Gd_2O_3). Tc onset and Tco were observed at 95^{o}K and 88^{o}K, respectively. This material can be represented by the stoichiometric formula $Y_{0.5}Gd_{0.5}Ba_2Cu_3O_{6-8}$.

EXAMPLE 9

The procedure of Example 7 was repeated but using 20-30% of Y and Yb substituted by Nb (introduced as Nb_2O_3). Tc onset was elevated further by 6-10^{o}K.

The invention is not limited to the above exemplified materials and many modifications and variations may be used. For example, superconducting ceramics can be formed also in thin films by dissolving the powder of raw materials which have been baked, in a solvent, and applying to a substrate in the form of the solution. Then, the coated substrate can be baked in oxidizing surroundings, and finally baked in reducing surroundings.